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PATENT SPECIFICATION

NO DRAWINGS

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Inventor: GERALD BOOTH

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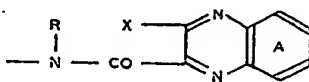
COMPLETE SPECIFICATION

Reactive Dyestuffs containing a Quinoxaline Nucleus

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to new dyestuffs and more particularly it relates to new dyestuffs which are valuable for colouring textile materials, in particular cellulose and woolen textile materials.

According to the invention there are provided the dyestuffs which contain attached to a carbon atom present in the dyestuffs at least one group of the formula:—



Formula I

wherein R represents a hydrogen atom or an alkyl radical containing from 1 to 4 carbon atoms; X represents a chlorine or a bromine atom or a $\text{—SO}_2\text{M}$ group wherein M represents a sodium or potassium atom; and the benzene ring A can contain further substituents.

Each of the groups of Formula I is attached to a carbon atom present in the dyestuffs. The said carbon atom may form part of an aryl residue present in the dyestuffs or may form part of an alkyl chain which is directly attached to an aryl residue present in the dyestuffs or which is attached to an aryl residue through a bridging atom or group. The dyestuffs may be members of any of the known series of dyestuffs but preferably they are dyestuffs of the azo, which may be monoazo or polyazo, nitro, anthraquinone or phthalocyanine series. If desired the dyestuffs, particularly the dyestuffs of the azo or phthalocyanine series, can contain coordinately bound metal atoms such as coordinately bound copper, cobalt or chromium atoms. The dyestuffs preferably contain at least one water-solubilising group such as a carboxylic acid and, above all, a sulphonc acid group.

As examples of the alkyl radicals represented by R there may be mentioned methyl and ethyl radicals; it is however preferred that R represents a hydrogen atom.

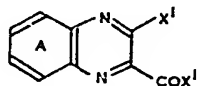
As examples of substituents which may be attached to the benzene ring A there may be mentioned halogen atoms such as chlorine, lower alkyl radicals such as the methyl radical, lower alkoxy radicals such as the methoxy radical, and nitro groups.

Throughout this Specification the terms "lower alkyl" and "lower alkoxy" are used to denote alkyl and alkoxy radicals respectively containing from 1 to 4 carbon atoms.

According to a further feature of the invention there is provided a process for the manufacture of the dyestuffs, as hereinbefore defined, wherein X represents a chlorine

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or a bromine atom which comprises reacting a dyestuff compound which contains at least one —NHR group with a compound of the formula: —



Formula II

wherein A has the meaning stated above, and X¹ represents a chlorine or a bromine atom, at least one molecular proportion of the said compound being used for each —NHR group present in the dyestuff compound.

The process of the invention may be conveniently brought about by stirring the reactants together in water, or in a water-miscible organic liquid, or in a mixture of water and a water-miscible organic liquid, preferably at a temperature between 0° and 50°C., whilst maintaining the mixture neutral by the addition of an acid-binding agent. At the conclusion of the reaction the resultant dyestuff is isolated by conventional methods.

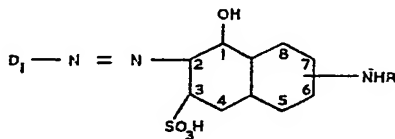
The compounds of Formula II may themselves be obtained by treating the corresponding compound of Formula II wherein X¹ represents an —OH group with a chlorinating or brominating agent, for example phosphorus oxychloride, phosphorus oxybromide, phosphorus pentachloride or phosphorus pentabromide.

As specific examples of the compounds of Formula II there may be mentioned 2-chloroquinoxaline-3-carbonyl chloride, 2-bromoquinoxaline-3-carbonyl bromide, 2-chloro-6-methylquinoxaline-3-carbonyl chloride, and 2-chloro-6-nitroquinoxaline-3-carbonyl chloride.

The dyestuff compounds used in the process of the invention may be any dyestuff compounds which contain at least one —NHR group, and such compounds may be obtained by the methods which are known for preparing dyestuff compounds containing amino or alkylamino groups.

As specific examples of dyestuff compounds containing at least one —NHR group, as hereinbefore defined, there may be mentioned the compounds of the following classes without, however, limiting the classes to those specifically described.

1. Monoazo compounds of the formula: —



(III)

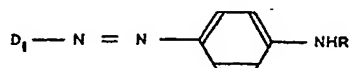
wherein D₁ represents a mono- or di-cyclic aryl radical which is free from azo groups and NHR groups, the —NHR group being preferably attached to the 6-, 7- or 8-position of the naphthalene nucleus, which may also contain a sulphonic acid group in the 5- or 6-position of the naphthalene nucleus.

D₁ may represent a radical of the naphthalene or benzene series which is free from azo substituents, for example a stilbene, diphenyl, benzthiazolylphenyl or diphenylamine radical. Also in this class are to be considered the related dyestuffs in which the NHR group, instead of being directly attached to the naphthalene nucleus, is attached to a benzoylamino or anilino group which is itself attached to the 6-, 7- or 8-position of the naphthalene nucleus.

Particularly valuable dyestuffs are obtained from those compounds wherein D₁ represents a sulphonated phenyl or naphthyl radical, especially those which contain a —SO₃H group in ortho position to the azo link; the phenyl radical may be further substituted for example, by halogen atoms such as chlorine, alkyl radicals such as methyl, acylamino groups such as acetylamino and alkoxy radicals such as methoxy.

2. Disazo compounds of formula III, wherein D₁ stands for a radical of the azobenzene, azonaphthalene or phenylazonaphthalene series and the naphthalene nucleus is substituted by the NHR group, and optionally by sulphonic acid as in class 1.

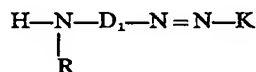
3. Monoazo compounds of the formula:—



(IV)

wherein D_1 stands for a mono- or di-cyclic aryl radical as described for class 1, and is preferably a disulphonaphthyl or a stilbene radical, and the benzene nucleus may contain further substituents such as halogen atoms, or alkyl, alkoxy, carboxylic acid and acylamino groups.

4. Mono- or dis-azo compounds of the formula:—



V

wherein D_1 represents an arylene radical such as a radical of the azobenzene, azonaphthalene or phenylazonaphthalene series, or, preferably, a mono- or dicyclic arylene radical of the benzene or naphthalene series, and K represents the radical of a naphthol sulphonic acid or the radical of an enolised or enolisable ketomethylene compound (such as an acetoacetyluride or a 5 - pyrazolone) having the OH group *o* to the azo group. D_1 preferably represents a radical of the benzene series containing a sulphonic acid group.

5. Mono or di-azo compounds of the formula:—

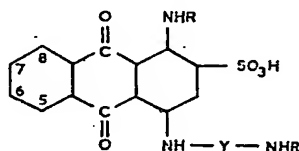


(VI)

wherein D_1 represents a radical of the types defined for D_1 in classes 1 and 2 above and K_2 represents the radical of an enolisable ketomethylene compound (such as an acetoacetyluride or a 5 - pyrazolone) having the —OH group in α -position to the azo group.

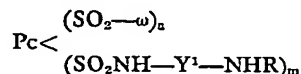
6. The metal complex, e.g. the copper, chromium and cobalt complex, compounds of those dyes of formulae III, V, and VI (wherein D_1 , K and K_2 have all the respective meanings stated) which contain a metallisable (for example, a hydroxyl, lower alkoxy or carboxylic acid) group *ortho* to the azo group in D_1 .

7. Anthraquinone compounds of the formula:—



wherein the anthraquinone nucleus may contain an additional sulphonic acid group in the 5-, 6-, 7- or 8-position and Y represents a bridging group which is preferably a di-valent radical of the benzene series, for example phenylene, diphenylene, or 4:4' - di-valent stilbene or azobenzene radicals. It is preferred that Y should contain one sulphonic acid group for each benzene ring present.

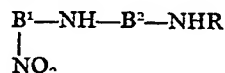
8. Phthalocyanine compounds of the formula:—



wherein Pc represents the phthalocyanine nucleus preferably of copper phthalocyanine, ω represents a hydroxy and/or an amino or substituted amino group, Y^1 represents a bridging group preferably an aliphatic, cycloaliphatic or aromatic bridging group, and

n and m each represent a value of from 1 to 3 and may be the same or different provided that $n + m$ is not greater than 4.

9. Nitro dyestuffs of the formula:—



5 wherein B^1 and B^2 represent monocyclic aryl nuclei, the nitro group in B^1 being *ortho* to the NH group. 5

In class 1

- 6 - amino - 1 - hydroxy - 2 - (2' - sulphophenylazo)naphthalene - 3 - sulphonic acid, 10
- 6 - methylamino - 1 - hydroxy - 2 - (4' - acetylamino - 2' - sulphophenylazo)naphthalene - 3 - sulphonic acid, 10
- 8 - amino - 1 - hydroxy - 2 - (2' - sulphophenylazo)naphthalene - 3:6 - disulphonic acid, 15
- 8 - amino - 1 - hydroxy - 2 - (4' - chloro - 2' - sulphophenylazo) - naphthalene - 3:5 - disulphonic acid, 15
- 7 - amino - 2 - (2':5' - disulphophenylazo) - 1 - hydroxynaphthalene - 3 - sulphonic acid, 20
- 7 - methylamino - 2 - (2' - sulphophenylazo) - 1 - hydroxynaphthalene - 3 - sulphonic acid, 20
- 7 - methylamino - 2 - (4' - methoxy - 2' - sulphophenylazo) - 1 - hydroxynaphthalene - 3 - sulphonic acid, 20
- 8 - (3' - aminobenzoylamino) - 1 - hydroxy - 2 - (2' - sulphophenylazo) - naphthalene - 3:6 - disulphonic acid, 25
- 8 - amino - 1 - hydroxy - 2:2' - azonaphthalene - 1':3:5' - 6 - tetrasulphonic acid, 25
- 8 - amino - 1 - hydroxy - 2:2' - azonaphthalene - 1':3:5' - trisulphonic acid, 30
- 6 - amino - 1 - hydroxy - 2:2' - azonaphthalene - 1':3:5' - trisulphonic acid, 30
- 6 - methylamino - 1 - hydroxy - 2:2' - azonaphthalene - 1':3:5' - trisulphonic acid, 30
- 7 - amino - 1 - hydroxy - 2:2' - azonaphthalene - 1':3 - disulphonic acid, 30
- 8 - amino - 1 - hydroxy - 2(4' - hydroxy - 3' - carboxyphenylazo) - naphthalene - 3:6 - disulphonic acid, 30
- 6 - amino - 1 - hydroxy - 2 - (4' - hydroxy - 3' - carboxyphenylazo) - naphthalene - 3:5 - disulphonic acid. 30

In class 2

- 8 - amino - 1 - hydroxy - 2 - [4' - (2'' - sulphophenylazo) - 2' - methoxy - 5' - methylphenylazo]naphthalene - 3:6 - disulphonic acid. 35
- 8 - amino - 1 hydroxy - [4' - (4'' - methoxyphenylazo) - 2' - carboxyphenylazo]naphthalene - 3:6 - disulphonic acid, 40
- 8 - amino - 1 - hydroxy - 2 - [4' - (2'' - hydroxy - 3''':6'' - disulpho - 1'' - naphthylazo) - 2' - carboxyphenylazo]naphthalene - 3:6 - disulphonic acid. 40
- 4:4' - bis(8'' - amino - 1'' - hydroxy - 3''':6'' - disulpho - 2'' - naphthylazo)-3:3 - dimethoxydiphenyl, 45
- 6 - amino - 1 - hydroxy - 2 - [4 - (2'' - sulphophenylazo) - 2' - methoxy - 5' - methylphenylazo]naphthalene - 3:5 - disulphonic acid. 45

In class 3

- 2 - (4' - amino - 2' - methylphenylazo)naphthalene - 4:8 - disulphonic acid, 50
- 2 - (4' - amino - 2' - acetylamino)phenylazo)naphthalene - 5:7 - disulphonic acid, 50
- 4 - nitro - 4' - (4'' - methylaminophenylazo)stilbene - 2:2' - disulphonic acid, 50
- 4 - nitro - 4' - (4'' - amino - 2'' - methyl - 5'' - methoxyphenylazo)stilbene - 2:2' - disulphonic acid, 50
- 4 - amino - 4' - (4'' - methoxyphenylazo)stilbene - 2:2' - disulphonic acid, 50
- 4 - amino - 2 - methylazobenzene - 2':5' - disulphonic acid. 50

In class 4

- 1 - (2':5' - dichloro - 4' - sulphophenyl) - 3 - methyl - 4 - (3'' - amino - 4'' - sulphophenylazo) - 5 - pyrazolone,
 5 1 - (4' - sulphophenyl) - 3 - carboxy - 4 - (4'' - amino - 3'' - sulphophenylazo) - 5 - pyrazolone, 5
 1 - (2' - methyl - 5' - sulphophenyl) - 3 - methyl - 4 - (4'' - amino - 3'' - sulphophenylazo) - 5 - pyrazolone,
 1 - (2' - sulphophenyl) - 3 - methyl - 4 - (3'' - amino - 4'' - sulphophenylazo) - 5 - pyrazolone,
 10 4 - amino - 4' - (3'' - methyl - 1'' - phenyl - 4'' - pyrazol - 5'' - onylazo)stilbene - 2:2' - disulphonic acid, 10
 4 - amino - 4' - (2'' - hydroxy - 3'' : 6'' - disulpho - 1'' - naphthylazo)stilbene - 2:2' - disulphonic acid,
 15 8 - acetyl amino - 1 - hydroxy - 2 - (3' - amino - 4' - sulphophenylazo)naphthalene - 3:6 - disulphonic acid, 15
 7 - (3' - sulphophenyl amino) - 1 - hydroxy - 2 - (4' - amino - 2' - carboxyphenylazo)naphthalene - 3 - sulphonic acid,
 8 - amino - 1 - hydroxy - 2,4' - hydroxy - 3' - carboxyphenylazo) - naphthalene - 3:6 - disulphonic acid,
 20 6 - acetyl amino - 1 - hydroxy - 2 - (5' - amino - 2' - sulphophenylazo)naphthalene - 3 - sulphonic acid. 20

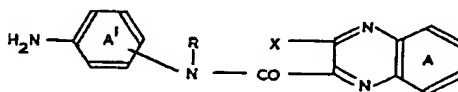
In class 5

- 1 - (3' - aminophenyl) - 3 - methyl - 4 - (2':5': - disulphophenylazo) - 5 - pyrazolone,
 25 1 - (3' - aminophenyl) - 3 - carboxy - 4 - (2' - carboxy - 4' - sulphophenylazo) - 5 - pyrazolone, 25
 4 - amino - 4' - [3'' - methyl - 4'' - (2''' : 5''' - disulphophenylazo) - 1'' - pyrazol - 5'' - onyl]stilbene - 2:2' - disulphonic acid,
 30 1 - (3' - aminophenyl) - 3 - carboxy - 4 - [4'' - (2''' : 5''' - disulphophenylazo) - 2'' - methoxy - 5'' - methylphenylazo] - 5 - pyrazolone. 30

In class 6

- The copper complex of 8 - amino - 1 - hydroxy - 2 - (2' - hydroxy - 5' - sulphophenylazo)naphthalene - 3:6 - disulphonic acid,
 35 The copper complex of 6 - amino - 1 - hydroxy - 2 - (2' - hydroxy - 5' - sulphophenylazo)naphthalene - 3 - sulphonic acid, 35
 The copper complex of 6 - amino - 1 - hydroxy - 2 - (2' - hydroxy - 5' - sulphophenylazo)naphthalene - 3:5 - disulphonic acid,
 The copper complex of 8 - amino - 1 - hydroxy - 2 - (2' - hydroxy - 3' - chloro - 5' - sulphophenylazo)naphthalene - 3:6 - disulphonic acid,
 40 The copper complex of 6 - methyl amino - 1 - hydroxy - 2 - (2' - carboxy - 5' - sulphophenylazo)naphthalene - 3 - sulphonic acid, 40
 The copper complex of 8 - amino - 1 - hydroxy - 2 - [4' - (2'' - sulphophenylazo) - 2' - methoxy - 5' - methylphenylazo]naphthalene - 3:6 - disulphonic acid.
 The copper complex of 6 - amino - 1 - hydroxy - 2 - [4' - (2'' : 5'' - disulphophenylazo) - 2' - methoxy - 5' - methylphenylazo] - naphthalene - 3:5 - disulphonic acid,
 45 The copper complex of 1 - (3' - amino - 4' - sulphophenyl) - 3 - methyl - 4 - [4'' - (2''' : 5''' - disulphophenylazo) - 2'' - methoxy - 5'' - methylphenylazo] - 5 - pyrazolone, 45
 50 The copper complex of 7 - (4' - amino - 3' - sulphoanilino) - 1 - hydroxy - 2 - [4'' - (2''' : 5''' - disulphophenylazo) - 2'' - methoxy - 5'' - methylphenylazo]naphthalene - 3 - sulphonic acid, 50
 The copper complex of 6 - (4' - amino - 3' - sulphoanilino) - 1 - hydroxy - 2 - (2'' - carboxyphenylazo)naphthalene - 3 - sulphonic acid,
 55 The 1:2 - chromium complex of 7 - amino - 6' - nitro - 1:2' - dihydroxy - 2:1' - azonaphthalene - 3:4' - sulphonic acid, 55
 The 1:2 - chromium complex of 6 - amino - 1 - hydroxy - 2 - (2' - carboxyphenylazo)naphthalene - 3 - sulphonic acid,
 The 1:2 - chromium complex of 8 - amino - 1 - hydroxy - 2 - (4' - nitro - 2' - hydroxyphenylazo)naphthalene - 3:6 - disulphonic acid,
 60 The 1:2 - cobalt complex of 6 - (4' - amino - 3' - sulphoanilino) - 1 - hydroxy - 2 - (5'' - chloro - 2'' - hydroxyphenylazo)naphthalene - 3 - sulphonic acid, 60

- The 1:2 - chromium complex of 1 - (3' - amino - 4' - sulphophenyl) - 3 - methyl - 4 - (2'' - hydroxy - 4'' - sulphonyl - 1'' - naphthylazo) - 5 - pyrazolone,
 The 1:2 - chromium complex of 7 - (4' - sulphoanilino) - 1 - hydroxy - 2 - (4'' - amino - 2'' - carboxyphenylazo)naphthalene - 3 - sulphonic acid.
 5 The 1:2 - chromium complex of 1 - (3' - aminophenyl) - 3 - methyl - 4 - (4'' - nitro - 2'' - carboxyphenylazo) - 5 - pyrazolone. 5
- In class 7*
 1 - amino - 4 - (3' - amino - 4' - sulphoanilino)anthraquinone - 2 - sulphonic acid,
 10 1 - amino - 4 - (4' - amino - 3' - sulphoanilino)anthraquinone - 2:5 - disulphonic acid, 10
 1 - amino - 4 - [4' - (4'' - amino - 3'' - sulphophenyl)anilino]anthraquinone - 2:5 - disulphonic acid,
 15 1 - amino - 4 - [4'' - amino - 2'' - sulphophenylazo]anilino] - anthraquinone - 2:5 - disulphonic acid, 15
 1 - amino - 4 - (4' - methylamino - 3' - sulphoanilino)anthraquinone - 2 - sulphonic acid.
- In class 8*
 20 3 - [(3' - amino - 4' - sulphophenyl)sulphamyl] copper phthalocyanine - tri - 3 - sulphonic acid, 20
 Di - 4 - [(3' - amino - 4' - sulphophenyl)sulphamyl] copper phthalocyanine - di - 4 - sulphonic acid,
 3 - (3' - aminophenylsulphamyl) - 3 - sulphamyl copper phthalocyanine - di - 3 - sulphonic acid.
- 25 *In class 9* 25
 4 - amino - 2' - nitro - diphenylamine - 3:4' - disulphonic acid.
- According to a further feature of the invention there is provided a process for the manufacture of the dyestuffs as hereinbefore defined, wherein X represents a —SO₃M group which comprises reacting a dyestuff wherein X represents a chlorine or a bromine atom with a sodium or potassium salt of sulphurous acid.
 30 The alternative process of the invention may be conveniently brought about by stirring the reactants together in water or in a mixture of water and a water - miscible organic liquid, preferably at a temperature between 20° and 100°C., and isolating the resulting dyestuff by conventional methods. 30
 35 As specific examples of the said salts of sulphurous acid there may be mentioned sodium sulphite, sodium bisulphite and potassium sulphite. 35
 Alternatively the dyestuffs of the invention can be obtained by the methods known to be capable of converting dyestuff intermediates into dyestuffs, at least one of the said intermediates containing a group or groups of Formula I. The word "known" is to be understood as designating methods in actual use as described in literature on the subject.
 40 Thus for example dyestuff intermediates containing reactive halogen atoms, such as 1 - amino - 4 - bromoanthraquinone - 2 - sulphonic acid, phthalocyanine sulphonyl-chlorides, in particular copper phthalocyanine 3- or 4 - mono-, di- or tri-sulphonyl-chloride, can be reacted with amines containing a group of Formula I, such as an amine of the formula:— 45



Formula VII

wherein A, R and X have the meanings stated, and the benzene ring A' can be substituted by halogen atoms or methyl, methoxy or sulphonic acid groups.

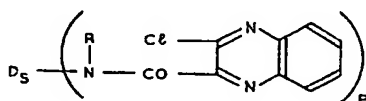
- 50 The azo dyestuffs of the invention can also be obtained by diazotising a primary aromatic amine and coupling the resulting diazo compound with a coupling component, the primary aromatic amine and the coupling component together containing at least one group of Formula I. 50

The said primary aromatic amines may be members of any of the known series of diazotisable amines but preferably they are diazotisable aromatic amines of the benzene or naphthalene series. Such aromatic amines containing a group of Formula I (such as the amines of Formula VII) wherein X represents a chlorine or a bromine atom may themselves be obtained by reacting the corresponding amine or nitro compound containing a —NHR group with a compound of Formula II and subsequently reducing the nitro group to an amino group.

The said coupling components may be members of any of the known series of coupling components, but preferably they are coupling components of the phenol, naphthol, acetoacetylamine, naphthylamine, 5 - aminopyrazole or 5 - pyrazolone series. Coupling components containing a group of Formula I wherein X represents a chlorine or a bromine atom may themselves be obtained by reacting the corresponding coupling component containing a —NHR group with a compound of Formula II.

Aromatic amines or coupling components containing a group of Formula I wherein X represents $-\text{SO}_3\text{M}$ may themselves be obtained by treating with sodium or potassium sulphite the corresponding compounds containing a group of Formula I wherein X is a chlorine atom.

A preferred class of the dyestuffs of the invention are the dyestuffs which are represented by the formula:—



wherein R has the meaning stated, p represents 1 or 2, and D_s represents a dyestuff radical of the azo, anthraquinone or phthalocyanine series which contains at least one sulphonic acid or carboxylic acid group.

The new dyestuffs, as hereinbefore defined, are valuable for colouring natural and artificial textile materials for example textile materials comprising cotton, viscose rayon, regenerated cellulose, wool, silk, cellulose acetate, polyamides, polyacrylonitrile, modified polyacrylonitrile, and aromatic polyester fibres. For this purpose the dyestuffs can be applied to the textile materials by dyeing, padding or printing processes, using in the latter case printing pastes containing the conventional thickening agents or oil-in-water emulsions or water - in - oil emulsions, whereby the textile materials are coloured in bright shades possessing excellent fastness to light and to wet treatments such as washing.

The new dyestuffs which contain water-solubilising groups, for example sulphonic acid and carboxylic acid groups, which render them soluble in water are particularly valuable for colouring cellulose textile materials. For this purpose the dyestuffs are preferably applied to the cellulose textile material in conjunction with a treatment with an acid-binding agent, for example sodium carbonate, sodium metasilicate, trisodium phosphate or sodium hydroxide, which may be applied to the cellulose textile material before, during or after the application of the dyestuff. Alternatively when the dyed textile material is to be subsequently heated or steamed a substance, such as sodium bicarbonate or sodium trichloroacetate, can be used which on heating or steaming liberates an acid-binding agent.

For example the cellulose textile material can be coloured by treating the cellulose textile material with an aqueous solution or suspension of the acid-binding agent and then immersing the so - treated cellulose textile material in a dyebath comprising a solution of one or more of the new dyestuffs, as hereinbefore defined, at a temperature of between 0° and 100°C., removing the dyed cellulose textile material from the dyebath and if desired subjecting the dyed cellulose textile material to a treatment in a hot aqueous solution of soap.

If desired the cellulose textile material which has been treated with an aqueous solution or suspension of the acid - binding agent may be passed between rollers to remove excess aqueous solution or suspension of the acid - binding agent and/or dried before being treated with the aqueous solution of the said dvestuffs.

Alternatively the aqueous solution of the dyestuff may be applied by padding to the cellulose textile material which has been treated with the acid-binding agent and the cellulose textile material then passed through rollers and subsequently subjected to the action of heat or steam. Alternatively the cellulose textile material can be padded with an aqueous solution of one or more of the new dyestuffs, as hereinbefore defined, which solution also contains an acid - binding agent, passing the so - treated cellulose textile material through rollers, then if desired drying the cellulose textile

- material at a suitable temperature, for example 70°C., and then subjecting the cellulose textile material to the action of heat or steam. Alternatively the cellulose textile material can be dyed by immersing it in a dyebath comprising an aqueous solution of one or more of the said dyestuffs which solution also contains an acid-binding agent, at a suitable temperature for example between 0° and 100°C., and thereafter removing the cellulose textile material from the dyebath, if desired subjecting it to a treatment in a hot aqueous solution of soap and finally drying the dyed cellulose textile material. Alternatively the aqueous solution of one or more of the said dyestuffs can be applied to the cellulose textile material by a dyeing or a padding method and the coloured cellulose textile material subsequently immersed in an aqueous solution or suspension of the acid-binding agent, preferably at a temperature between 50°C. and 100°C., or alternatively the coloured cellulose textile material may be padded with an aqueous solution or suspension of the acid - binding agent, the textile material dried and then subjected to the action of heat or steam. Alternatively the cellulose textile material can be dyed by immersing it in a dyebath comprising an aqueous solution of one or more of the said dyestuffs, preferably at a temperature between 20° and 100°C., and, after the textile material has absorbed some or all of the dyestuffs, adding an acid - binding agent and proceeding with the dyeing at the same or a different temperature.
- The concentration of the acid - binding agent present in the aqueous solution of the dyestuffs is not critical but it is preferred to use between 0.1% and 10% of the acid-binding agent based on the total weight of the aqueous solution. If desired the aqueous solution or suspension of the acid - binding agent may also contain further substances, for example electrolytes such as sodium chloride and sodium sulphate.
- The aqueous solution of one or more of the said dyestuffs may also contain substances which are known to assist the application of dyestuffs to textile materials, for example sodium chloride, sodium sulphate, urea, dispersing agents, surface - active agents, sodium alginate or an emulsion of an organic liquid, for example trichloroethylene in water.
- Alternatively the cellulose textile materials can be printed with a printing paste containing one or more of the new dyestuffs of the invention.
- This may be conveniently brought about by applying a printing paste containing one or more of the said dyestuffs, to a cellulose textile material which has been impregnated with an acid - binding agent and thereafter subjecting the printed cellulose textile material to the action of heat or steam. Alternatively a printing paste containing one or more of the said dyestuffs and containing an acid - binding agent can be applied to the cellulose textile material and the printed cellulose textile material subsequently subjected to the action of heat or steam. Alternatively a printing paste containing one or more of the said dyestuffs can be applied to the cellulose textile material which is subsequently immersed in a hot aqueous solution or suspension of the acid-binding agent or alternatively the printed textile material is impregnated with an aqueous solution or suspension of the acid-binding agent and subsequently subjected to the action of heat or steam.
- After applying the printing paste to the cellulose textile material the printed textile material may, if desired, be dried, for example at a temperature between 20° and 100°C. before the printed textile material is subjected to the action of heat or steam.
- The cellulose textile material may be printed with the printing paste by any of the commonly known methods of applying printing pastes to textile materials, for example by means of roller printing, screen printing, block printing, spray printing or stencil printing. The printing pastes may also contain the commonly used adjuvants, for example urea, thickening agents, for example methyl cellulose, starch, locust bean gum, sodium alginate, water-in-oil emulsions, oil-in-water emulsions, surface-active agents, sodium *m* - nitrobenzene sulphonate, and organic liquids, for example ethanol.
- At the conclusion of the dyeing and/or printing processes it is preferred to subject the so-coloured cellulose textile materials to a "soaping" treatment, which may be carried out by immersing the coloured cellulose textile materials for a short time, for example 15 minutes, in a hot aqueous solution of soap and/or detergent, and subsequently rinsing the coloured textile material in water before drying it.
- Those new dyestuffs which do not contain water - solubilising groups, for example sulphonic acid, carboxylic acid, sulphonamide and acylsulphonamide groups are, in general, applied to textile materials in the form of an aqueous dispersion which may be obtained by gravel-milling the dyestuff with water in the presence of a dispersing agent, for example the sodium salt of sulphonated naphthalene formaldehyde condensation products, sulphosuccinic acid esters, Turkey Red Oil, alkyl phenol/ethylene oxide condensation products, soap and similar surface-active materials with or without protective

colloids such as dextrin, British gum and water-soluble proteins. If desired the aqueous paste of the dyestuff so obtained may be dried to form a re-dispersible powder which may be converted to a non-dusting powder by any of the processes known for forming non-dusting powders.

The new dyestuffs, as hereinbefore defined, can be applied to nitrogen-containing textile materials such as wool and polyamide textile materials, from a mildly alkaline, neutral or acid dyebath. The dyeing process can be carried out at a constant or substantially constant pH, that is to say the pH of the dyebath remains constant or substantially constant during the dyeing process, or if desired the pH of the dyebath can be altered at any stage of the dyeing process by the addition of acids or acid salts or alkalis or alkaline salts. For example dyeing may be started at a dyebath pH of about 3.5 to 5.5 and raised during the dyeing process to about 6.5 or 7.5 or higher if desired. The dyebath may also contain substances which are commonly used in the dyeing of nitrogen-containing textile materials. As example of such substances there may be mentioned ammonium acetate, sodium sulphate, ethyl tartrate, non-ionic dispersing agents such as condensates of ethylene oxide with amines, fatty alcohols or phenols, surface-active cationic agents such as quaternary ammonium salts for example cetyl trimethyl-ammonium bromide and cetyl pyridinium bromide and organic liquids such as *n*-butanol and benzyl alcohol.

The invention is illustrated but not limited by the following Examples in which the parts and percentages are by weight.

EXAMPLE 1

A solution of 9.3 parts of the trisodium salt of 1 - (4' - sulphophenyl) - 3 - carboxy - 4 - (3' - amino - 4' - sulphophenylazo) - 5 - pyrazolone in 200 parts of water is added to a suspension of 4.15 parts of 2 - chloroquinoxaline - 3 - carbonyl chloride in a mixture of 200 parts of water and 40 parts of ice, and the resulting mixture is stirred at 5° to 10°C. until no further additions of sodium carbonate are required to maintain the pH at 6. 100 parts of sodium chloride are then added and the precipitated dyestuff is filtered off and dried.

On analysis the dyestuff is found to contain 0.9 atom of organically bound chlorine per molecule. When applied to cellulose textile materials in conjunction with a treatment with an acid-binding agent or to wool the dyestuff yields yellow shades possessing excellent fastness to light, to washing and to acids and alkalis.

EXAMPLE 2

A solution of 4.15 parts of 2 - chloroquinoxaline - 3 - carbonyl chloride in 100 parts of acetone is added to a solution of 5.3 parts of the sodium salt of 1 - amino - 8-naphthol - 3:6 - disulphonic acid in 300 parts of water at 20° C., and the resulting mixture is stirred for 30 minutes at 10° C. The pH of the mixture is then raised to 7 by the addition of sodium carbonate, and an aqueous solution of diazotised aniline - 2 - sulphonic acid (obtained by diazotising 2.9 parts of aniline - 2 - sulphonic acid by known methods) is added. Sodium carbonate is then added to raise the pH to 7.5 and the mixture is stirred for 3 hours at 10°C. Sodium chloride is then added to precipitate the dyestuff which is filtered off and dried.

On analysis the dyestuff is found to contain 1 atom of organically bound chlorine per molecule. When applied to cellulose textile materials in conjunction with a treatment with an acid - binding agent the dyestuff yields bluish-red shades possessing excellent fastness to light, to washing, to acids and to alkalis.

EXAMPLE 3

24 parts of copper phthalocyanine - 3 - [sulphon - N - (3' - aminophenyl) amide]_{1.0} - 3 - (sulphonamide)_{1.0} - 3 - (sulphonic acid)_{2.0} (which may be obtained by the method described in Example 96 of British Specification No. 927773) are suspended in 400 parts of water, and an aqueous solution of sodium hydroxide is added until a clear solution of pH 7 is obtained. The solution is cooled to 5°C., and a solution of 7.1 parts of 2 - chloro - quinoxaline - 3 - carbonyl chloride in 100 parts of acetone is then added during 30 minutes, whilst maintaining the pH between 6.5 and 7 and by the addition of an aqueous solution of sodium hydroxide. The resulting mixture is then stirred for 1 hour at 20°C., 100 parts of sodium chloride are added, and the precipitated dyestuff is filtered off and dried.

When applied to cellulose textile materials by a printing process using a print paste which also contains an acid - binding agent the dyestuff yields greenish - blue prints possessing excellent fastness to wet treatments and to light.

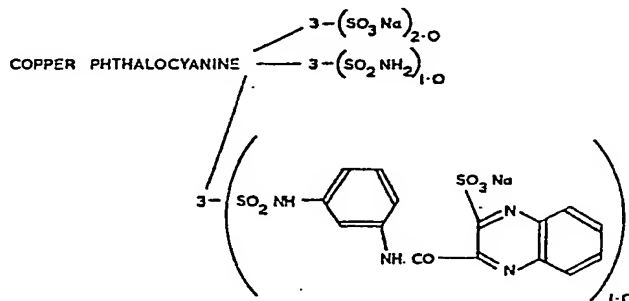
EXAMPLE 4

In place of the copper phthalocyanine derivative used in Example 3 there are used 24 parts of copper phthalocyanine - 3 - [sulpho - N - (3' - amino phenyl)amide]₁ - 3 - (sulphonic acid)₃ when a similar dyestuff is obtained.

EXAMPLE 5

A mixture of 8 parts of the dyestuff of Example 3, 2 parts of sodium sulphite and 250 parts of water is stirred for 1 hour at the boil under a reflux condenser. The resulting solution is cooled to 20°C., 25 parts of sodium chloride are added, and the precipitated dyestuff is filtered off and dried.

The resulting dyestuff consists essentially of the dyestuff of the formula:—



The properties of the dyestuff are similar to those of the dyestuff of Example 3.

EXAMPLE 6

A solution of 8.5 parts of 2 - chloroquininoxaline - 3 - carbonyl chloride in 150 parts of acetone is added to a solution of 16 parts of the trisodium salt of 1 - amino 4 - (3' - sulfo - 4' - aminoanilino)anthraquinone - 2:5 - disulphonic acid in a mixture of 300 parts of water and 50 parts of acetone at 5°C., and the resulting mixture is stirred for 1 hour at 0° to 10°C. The precipitated dyestuff is then filtered off, washed with a 5% aqueous solution of sodium chloride, then with acetone, and is finally dried.

On analysis the dyestuff is found to contain one atom of organically bound chlorine per molecule of dyestuff.

When applied to cellulose textile materials in conjunction with a treatment with an acid-binding agent the dyestuff yields blue shades possessing excellent fastness to light and to wet treatments.

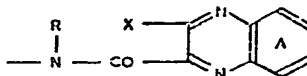
EXAMPLE 7

A solution of 2.45 parts of 2 - chloroquininoxaline - 3 - carbonyl chloride in 50 parts of acetone is added to a solution of 2.27 parts of 2 - hydroxy - 5 - methyl - 4' - amino-benzene in a mixture of 70 parts of acetone and 30 parts of water, and the mixture is stirred at 0° to 5°C. while 20 parts of a N aqueous solution of sodium carbonate are gradually added to maintain the pH of the mixture between 7 and 8. The mixture is then stirred for 20 hours at 20°C., and the precipitated dyestuff is filtered off, washed with water and dried.

When dispersed in aqueous medium the dyestuff dyes polyamide textile materials in yellow shades possessing excellent fastness to light and to washing.

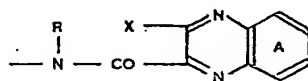
WHAT WE CLAIM IS:—

1. Dyestuffs which contain attached to a carbon atom present in the dyestuffs at least one group of the formula:—



wherein R represents a hydrogen atom or an alkyl radical containing from 1 to 4 carbon atoms; X represents a chlorine or a bromine atom or a —SO₃M group wherein M represents a sodium or potassium atom; and the benzene ring A can contain further substituents.

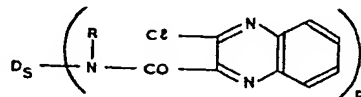
2. Azo, anthraquinone or phthalocyanine dyestuffs which contain attached to a carbon atom present in the dyestuffs at least one group of the formula:—



5 wherein R represents a hydrogen atom or an alkyl radical containing from 1 to 4 carbon atoms; X represents a chlorine or a bromine atom or a $-\text{SO}_3\text{M}$ group wherein M represents a sodium or potassium atom; and the benzene ring A can contain further substituents. 5

3. Dyestuffs as claimed in Claims 1 or 2 which contain at least one sulphonic acid group.

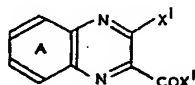
10 4. Dyestuffs, as claimed in any of Claims 1 to 3, which are represented by the formula:— 10



15 wherein R represents a hydrogen atom or an alkyl radical containing from 1 to 4 carbon atoms; p represents 1 and 2; and D_s represents a dyestuff radical of the azo, anthraquinone or phthalocyanine series which contains at least one sulphonic acid or carboxylic acid group. 15

5. Dyestuffs as claimed in any of Claims 1 to 4 as hereinbefore particularly described especially with reference to any of the Examples.

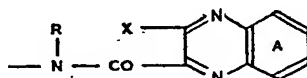
20 6. Process for the manufacture of the dyestuffs as claimed in Claim 1 wherein X represents a chlorine or a bromine atom, which comprises reacting a dyestuff compound which contains at least one $-\text{NHR}$ group with a compound of the formula:— 20



25 wherein A and R have the meanings stated in Claim 1, and X^1 represents a chlorine or a bromine atom, at least one molecular proportion of the said compound being used for each $-\text{NHR}$ group present in the dyestuff compound. 25

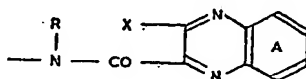
7. Process for the manufacture of the dyestuffs as claimed in Claim 1 wherein X represents a $-\text{SO}_3\text{M}$ group which comprises reacting a dyestuff as claimed in Claim 1 wherein X represents a chlorine or a bromine atom with a sodium or potassium salt of sulphurous acid.

30 8. Process for the manufacture of dyestuffs as claimed in Claim 1 which comprises reacting together dyestuff intermediates by the methods known to be capable of converting dyestuff intermediates into dyestuffs, at least one of the said intermediates containing a group of the formula:— 30



35 wherein A, R and X have the meanings stated in Claim 1. 35

9. Process for the manufacture of azo dyestuffs which contain attached to a carbon atom present in the dyestuffs at least one group of the formula:—



wherein A, R and X have the meanings stated in Claim 1, which comprises diazotising

a primary aromatic amine and coupling the resulting diazo compound with a coupling component, characterised in that the primary aromatic amine and the coupling component together contain at least one group of the above formula.

5 10. Process for the manufacture of dyestuffs as claimed in any of any of Claims 1 to 5 as hereinbefore particularly described especially with reference to any of the Ex-
amples. 5

11. Process for colouring textile materials which comprises applying to the textile material a dyestuff as claimed in any of Claims 1 to 5.

10 12. Process as claimed in Claim 11 wherein the textile material is a cellulose textile material and the application of the dyestuff is carried out in conjunction with a treatment with an acid-binding agent. 10

BERTRAM F. DREW,
Agent for the Applicants.

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